

Distinguishing opaline silica from cristobalite in bentonites: a practical procedure and perspective based on NaOH dissolution

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ABSTRACT: Respirable forms of crystalline silica including the mineral cristobalite are known carcinogens and the subject of increasing regulation and codes of good practice. Some bentonites may contain cristobalite, but more commonly they contain opal-CT, or opal-C, which can be confused with cristobalite. In the light of increasing regulation there is a clear need for simple and reliable methods that can distinguish cristobalite from the opals in bentonites and other clay materials. Here we propose the use of a simple NaOH method that is easily applied to bulk samples of bentonites. The method consists of boiling the clay in 0.5 M NaOH for 10 min and measuring the weight of undissolved solid. The method is shown to be accurate for both the identification and quantification of opal in bentonites since these phases are soluble when thus treated. It is also a straightforward method to distinguish the opals from cristobalite as the latter is essentially insoluble. Adoption by industry of a simple operationally-defined method such as this would be preferable to *ad hoc* reliance on direct instrumental methods alone such as X-ray powder diffraction, as the latter almost always require a large element of judgement and experience on the part of the analyst, although direct methods do need to be used in a supporting role.

KEYWORDS: crystalline silica, powder X-ray diffraction, cristobalite, opal-CT, bentonite, montmorillonite.

Interest in analytical methods for the quantitative determination of the amount of crystalline silica in a wide variety of materials has thrived in recent years due to the designation of respirable quartz and cristobalite as 'type 1' human carcinogens (IARC, 1997; NIOSH, 2002). The national and international regulations that followed this designation, such as the US Occupational Safety and Health Administration's (OSHA) hazard communication standard requiring the labelling of any product

containing 0.1% or more of crystalline silica, have prompted much discussion, evaluation and development of analytical methods. For example, a special issue of *Analytica Chimica Acta* was devoted to papers presented at an International Symposium entitled 'Issues and Controversy: the Measurement of Crystalline Silica' (Pardue, 1994).

As far as industrial clay materials are concerned, the most common form of crystalline silica, the mineral quartz, is almost invariably present in minor to trace amounts. The identification of quartz in clay materials is relatively straightforward by many techniques, as is its quantification, with techniques based on X-ray powder diffraction (XRPD) being by far the most widely used

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(Smith, 1997). Much more controversial, with respect to clay materials, is the identification and quantification of cristobalite. Cristobalite, a crystalline form of silica produced naturally and industrially at high temperatures (~1000°C), is the form at which regulation is directed. Unfortunately, the term cristobalite has also been used widely to refer to various opaline varieties of silica, which typically form at much lower temperatures. This dual use of the term to refer to different forms of silica is the source of much confusion. Smith (1998), who argued forcibly that forms of opaline silica should not be equated with crystalline cristobalite, discussed this problem in detail. This latter work focused on suggesting that the 'crystalline silica' regulations should not be applied to opals, because they are not crystalline but paracrystalline.

Bentonites are without doubt the clay materials most affected by this controversy since they may potentially contain crystalline cristobalite, which is covered by regulation, and they commonly contain either opal-CT or opal-C, both of which are frequently misidentified as cristobalite. In their classic treatise on bentonites, Grim & Güven (1978) refer only to 'cristobalite' as a common component of many bentonites, and it is clear that these authors did not draw any distinction between crystalline cristobalite and the opals.

The nomenclature of opaline forms of silica (Graetsch, 1994) continues to follow that introduced by Jones & Segnit (1971). In this classification, opal-A refers to X-ray amorphous (A) forms of opal, that is, material without any three dimensional or two dimensional order; opal-CT refers to a form that is interpreted as a disordered stacking sequence of cristobalite and tridymite (CT) layers; and opal-C a disordered form where cristobalite (C) layers are predominant. There is also general agreement that all of the opaline forms of silica contain water (Florke *et al.*, 1991; Graetsch, 1994; Smith, 1998), whereas cristobalite does not. There does not, however, appear to be general agreement as to whether the term 'crystalline' should be applied to opal-CT and opal-C (Florke *et al.*, 1991; Graetsch, 1994; Smith, 1998). Smith (1998) argued that the opals should always be referred to as paracrystalline because their XRPD patterns cannot be indexed on a single unit-cell. However, many of the features of the XRPD patterns of the opals may be explained in terms of the concepts of crystallite size (Elzea & Rice, 1996) and mixed-layering as a form

of defect (Guthrie *et al.*, 1995). In many ways this is analogous to the diffraction effects shown by most clay minerals. Furthermore, materials may exist with characteristics that range all the way between opal-C on the one hand and cristobalite on the other (Nagase & Akizuki, 1997). It seems likely, therefore, that the crystalline vs. non-crystalline debate and attempts to classify on this basis will remain moot points.

From a pragmatic point of view, it is important to establish a reliable, and preferably simple, means to distinguish the various forms of opal from cristobalite. Elzea *et al.* (1994) presented some criteria based on XRPD data that may be useful in this respect, including a tabulation of the peak width values (full width at half maximum, FWHM) of the principal powder diffraction maxima of opal-CT, opal-C and cristobalite. They also indicate that the narrowing and shifting of the diffraction maxima of opals following heating to 1050°C for 24 h is a useful test for distinguishing opal from cristobalite, because the latter is unchanged following this treatment. Reliance on XRPD alone, however, may be inadequate in many instances, for example, cases where peak parameters are difficult to measure due to small concentration or interference from other phases; in bentonites, plagioclase feldspar is a common interference. There is also the possibility that both opal and cristobalite may be present in the same sample and since the principal diffraction maxima of both of these phases overlap the broader peaks of the opal may obscure the presence of cristobalite. This situation is not unlike the difficulty of distinguishing mica and illite by XRPD. The XRPD peak parameters are also instrument-dependent and, as a result, calibration would be required between different laboratories in order to apply an approach based on the measurement of XRPD peak parameters in a rigorous and reproducible fashion. Elzea *et al.* (1994) examined 20 different bentonites and clays and concluded that none of them contained the high-temperature form of cristobalite. Cristobalite, however, has been reported in volcanic rocks and ashes so frequently in the past that one must assume that it would be naïve to apply the conclusion of Elzea *et al.* (1994) quite generally to all bentonites. For example, the ash from the 1980 eruption of Mount St. Helens contains cristobalite (probably formed during slow cooling of lava from volcanic temperatures prior to its incorporation in the ash) and opal is also

reported (Pevear *et al.*, 1982). In another example, Mizota *et al.* (1987) presented convincing XRPD and oxygen-isotopic evidence that the cristobalite in soils derived from volcanic ash in the West Indies, Indonesia and Japan was crystalline cristobalite, formed at high temperatures and of volcanic origin. More recently, Baxter *et al.* (1999) described a cristobalite component (up to 24%) of volcanic ash from the Soufriere Hills volcano, Montserrat. Here cristobalite is believed to have formed by vapour phase crystallization and devitrification in a lava dome, the temperature of which is estimated at ~850°C, prior to its incorporation in the ashes of subsequent volcanic eruptions. The pertinent point is that, in almost all instances, bentonites are the products of the alteration of volcanic ash or volcanic rock. Hence it is clear that there is significant potential for the occurrence of cristobalite of volcanic origin in bentonite.

In addition to direct methods, chemical methods have also been used for the analysis of crystalline silica. Miles & Hamilton (1994) reviewed a variety of chemical methods and in a related paper Miles (1994) proposed the use of the National Institute of Occupational Safety and Health (NIOSH) method 7601 in combination with NIOSH method 7500 to distinguish between opaline and crystalline forms of silica. NIOSH 7601 is based on digestion in refluxing phosphoric acid and 7500 is based on XRPD. Both of these methods are designed to be applied to samples of a few milligrams, although, recently, phosphoric acid digestion was also used successfully to distinguish forms of silica in bulk bentonite samples (Önal *et al.*, 2006). Currently, the European Commission is considering the introduction of new legislation in relation to crystalline silica, including possible enlargement of the scope of the Directive on Carcinogens at Work (2004/37/EC). In the interim, some European industry employers and employee associations have signed a Social Dialogue agreement 'Agreement on Workers' Health Protection Through the Good Handling and Use of Crystalline Silica and Products Containing it'. The agreement is based around the adoption of a code of good practice, though some quarters have interpreted it as an effort to avoid further EU legislation (Musu & Sapir, 2006).

Against this background there is still a need for further research, including the development of analytical methods that may be used in support of any future regulations with respect to occupational

exposure limits (OELs), or in support of good practice. Manufacturers are interested in such processes so they can label their products accurately, as and when required, as well as make informed decisions about which bentonite or clay deposits to exploit. Here, we propose an alternative procedure to that followed by Miles (1994) or Önal *et al.* (2006) for the distinction between opaline silica and cristobalite. The procedure is based on NaOH dissolution and is both rapid and apparently more specific than phosphoric acid digestion. It is also designed to be applied to a 5 g sample of a bulk material, to increase the amount of sample analysed and to reduce the likelihood of serious gravimetric errors compared with NIOSH 7601.

MATERIALS

The samples used in this study, along with details of their origin, where known, are listed in Table 1. The samples include a variety of clay materials, and a variety of pure and mixed silica phases. Opal-3 is a sample of pure opal-CT from Virgin Valley Nevada, from the same source as that previously studied by Guthrie *et al.* (1995). The samples labelled Clay-A, Clay-B and Clay-C were obtained from the authors' participation in an informal round-robin on the 'Determination of quartz and cristobalite in bentonite' organized by the European Bentonite Producers Association (EUBA) and concluded in January 2005. These three samples were included in the present study since they were believed by the present authors to contain significant amounts of silica in the form of opal-CT and/or opal-C, although they were variously identified in the round-robin by different laboratories, sometimes as opals and sometimes as cristobalite. Samples RT7333, RT7495, and Pre-ship-T16, are also bentonites, obtained from CETCO, Europe Ltd. but contain silica of a more questionable identity. SWy-1, STx-1 and SAz-1 are reference smectites obtained from the Clay Minerals Society, Source Clay Repository, along with two kaolinites, KGa-2 and KGa-1b. Only one of these reference clays (STx-1) is known to contain opaline silica (Chipera & Bish, 2001). The samples labelled XPF4, XPF6, M72 and M3000 are essentially pure cristobalites formed at high temperatures industrially by the calcination of high-purity quartz sands. Sample DKS is the commercially available 'Deane K Smith' cristobalite, from the Gem Dugout, State College, PA

TABLE 1. Sample identification and origin/source.

Sample	Origin
46-E5888	Opal-CT, Virgin Valley, Nevada, Wards Natural Science
Clay-A	Chinese clay SHD
Clay-B	Turkish clay Peker
Clay-C	Greek clay White Prassa
RT7333	Cetco bentonite
RT7495	Cetco bentonite
Pre-ship-T16	Cetco bentonite
STx-1	STx-1 Ca-montmorillonite Source Clay Minerals Repository
SWy-1	SWy-1 Na-montmorillonite Source Clay Minerals Repository
SAz-1	SAz-1, Source Clay Minerals Repository
KGa-2	KGa-2 poorly crystallized kaolinite, Source Clay Minerals Repository
KGa-1b	KGa-1b well crystallized kaolinite, Source Clay Minerals Repository
XPF4	Cristobalite, XPF4 grade, WBB minerals
XPF6	Cristobalite, XPF6 grade, WBB minerals
M72	Cristobalite 'Sibelite' M72
M3000	Cristobalite 'Sibelite' M3000
DKS	Cristobalite standard, Gem Dugout
Cri-14	Cristobalite in obsidian, Coso Hot Springs, Inyo Co, California, Excalibur Minerals Co.
Sigma (S5631)	Quartz, Sigma-Aldrich
Minusil-15	Quartz, US Silica Company

16803, USA. The sample Cri-14, is a naturally occurring mixture of feldspar and cristobalite of presumed high-temperature origin from an obsidian volcanic glass. Additionally, two quartz samples were examined, one (S5631) available from Sigma-Aldrich, the other Min-U-Sil-15 available from the US Silica company, WV 25411, USA.

The particle-size distribution of the bentonites and other clay samples is unknown but all were powders. Two of the four industrial cristobalite samples, namely XPF4 and M72 were sands with mean particle sizes of $\sim 300 \mu\text{m}$, as measured by laser diffraction. The other two, XPF6 and M3000, were much finer grained 'flours' with mean particle-sizes of 14 and 17 μm , respectively, and both had a $< 2 \mu\text{m}$ fraction of $> 10 \text{ wt.}\%$. The manufacturers of Min-U-Sil-15 list it as nominally 100% $< 15 \mu\text{m}$ and similarly the Sigma-Aldrich quartz is listed as nominally 97–100% $< 8 \mu\text{m}$.

METHODS

NaOH dissolution

For each treatment, the samples were oven dried overnight at 105°C and allowed to re-equilibrate with the ambient laboratory atmosphere for 2 h to reach a stable moisture content. Five grams of each

sample were then weighed-out accurately using a four-place calibrated balance and transferred to a 1 l Pyrex glass beaker containing 500 ml of boiling 0.5 M NaOH. The beakers and their contents were covered with aluminium foil and boiled and stirred continuously with a magnetic stirrer for precisely 10 min. They were then cooled rapidly by immersion in cold water, allowed to clear by flocculation, and the sample recovered by removing the liquid using a combination of suction decantation and centrifugation. The recovered clay was again oven-dried, allowed to re-equilibrate and an accurate weight recorded. Note that Pyrex glass beakers were used for the dissolution experiments since they are readily available. Should chemical analysis of the supernatant for silica be required it would be pertinent to use an alternative such as Teflon or stainless steel, since NaOH may cause some dissolution of the glassware, although none was apparent and was of no concern in the present investigation.

XRPD

X-ray powder diffraction (XRPD) was made using a Siemens D5000 diffractometer and cobalt K-alpha radiation. Samples were run from 2–75°2 θ , with a step-size of 0.02° and counting time of 2 s

per step with a scintillation detector. The incident beam was collimated with a 1° divergence slit and soller slits, and the diffracted beam was collimated with 1° antiscatter slits, a 0.6 mm receiving slit and a graphite monochromator. For qualitative analysis, samples were ground by hand in a mortar and pestle and packed into holders, taking care as much as possible to avoid inducing any preferred orientation. For quantitative analysis, samples were McCrone-milled together with a 20 wt.% addition of corundum, and spray-dried directly from the mill as described by Hillier (2003). Quantitative analyses were made by a full pattern fitting reference intensity ratio (RIR) method (Participant 18–P18) as described in Omotoso *et al.* (2006). The standards used for this approach were obtained from the mineral collection of the Macaulay Institute and were measured as pure phase patterns and as 50:50 mixtures with corundum to obtain the relevant full pattern RIRs. Pattern fitting was made using the Solver function of Excel, allowing the patterns to scale with respect to intensity and with small shifts along 2θ accommodated by interpolation using a cubic spline function.

RESULTS

XRPD

Table 2 lists FWHM data for the peak at $\sim 4.05 \text{ \AA}$, where present, in the various samples. With respect to crystalline and para-crystalline silica phases, this peak may arise from opal-CT, opal-C or cristobalite. Although the criteria are by no means universally accepted, changes in peak shapes, peak widths and the presence or absence of certain peaks, form the basis by which these phases are identified and classified using XRPD data (Jones & Segnit, 1971; Graetsch, 1994). Applying the criteria of Elzea *et al.* (1994), for example, the respective bentonite and clay samples contain either opal-CT, or opal-C, but not cristobalite. Figure 1 shows the XRPD patterns of two of the samples that illustrate the range of diffraction patterns observed in the clay materials, namely Clay-B and RT7495. In Clay-B, the peak at $\sim 4.05 \text{ \AA}$ is very broad (FWHM = $0.954 \Delta^2\theta$) and no other peaks are obviously attributable to this phase in its admixture with smectite. In comparison, the 4.05 \AA peak in sample RT7495 is much sharper

TABLE 2. XRPD peak width (FWHM) data, XRPD quantitative analysis data (wt.%) and NaOH dissolution data (wt.%).

Sample	FWHM 4.05 \AA peak ($\Delta^2\theta$)	XRPD (%)	Starting weight (g)	Final weight (g)	% dissolved in NaOH
46-E5888	2.082	100	5.0018	0.3269	93.5
Clay-A	0.554	26.0	5.0006	3.6122	27.8
Clay-B	0.954	40.0	5.0018	3.0097	39.8
Clay-C	0.664	20.9	4.9998	4.0393	19.2
RT7333	0.296	23.4	5.0006	4.0477	19.1
RT7495	0.334	37.3	5.0001	3.5070	29.9
Pre-ship-T16	0.230	2.1	4.9989	4.9290	1.4
STx-1	0.739	19.3	4.9994	4.1334	17.3
SWy-1	NA	NA	5.0056	5.0410	-0.7
SAz-1	NA	NA	4.9987	4.8149	3.7
KGa-2	NA	NA	4.9999	4.4354	11.3
KGa-1b	NA	NA	4.9993	4.6508	7.0
XPF4	0.287	100	4.9993	4.9152	1.7
XPF6	0.272	100	5.0061	4.4191	11.7
M72	0.237	100	4.9993	5.0042	-0.1
M3000	0.230	100	5.0047	4.6983	6.1
DKS	0.185	100	4.9984	4.9819	0.3
Cri-14	0.273	40.0	4.9936	4.8665	2.5
Sigma (S5631)	NA	100	4.9948	4.9261	1.4
Minusil-15	NA	100	5.0005	4.9269	1.5

NA = not applicable (no 4.05 \AA peak present).

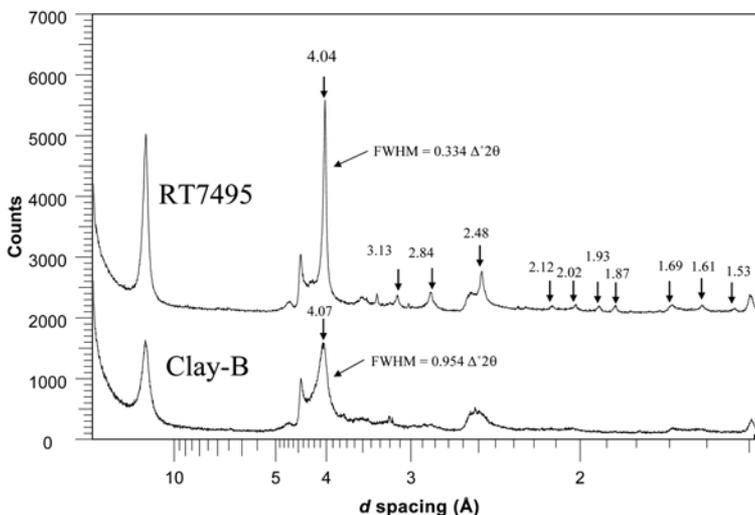


Fig. 1. XRPD patterns of samples Clay B and RT7495. According to the FWHM criteria of Elzea *et al.* (1994) Clay-B contains opal-CT, with the peak at ~ 4.05 Å being the only peak clearly attributable to this phase, other peaks being difficult to resolve from the background and/or peaks due to dioctahedral smectite. RT7495, contains opal-C, with at least 10 relatively sharp peaks recognizable in the range shown.

(FWHM = $0.334 \Delta^\circ 2\theta$) and shows at least ten additional peaks, including those at ~ 3.13 , 2.83 , 2.48 , 2.12 , 2.02 , 1.93 , 1.87 , 1.69 , 1.61 and 1.53 Å. As for the industrial cristobalites, apart from the Gem Dugout reference sample, quite surprisingly all have FWHM values that fall within the range given by Elzea *et al.* (1994) for opal-C (0.222 – $0.453 \Delta^\circ 2\theta$) rather than cristobalite (0.109 – $0.140 \Delta^\circ 2\theta$).

Table 2 also includes data for the quantitative analysis by full pattern fitting of the XRPD data of the clay samples. These data show that the 4.05 Å phase may account for as much as 40 wt.% of some of the bentonite samples. An example of the full pattern fitting is shown in Fig. 2. Additionally, the industrial cristobalites and the reference opal-CT shown in Table 2 are assumed to be 100% pure, although minor quartz impurity was evident in some.

Treatment of the pure opal-CT by NaOH showed that it was almost completely dissolved, losing 93.5% of its starting mass. For the bentonites, NaOH dissolution generally resulted in weight losses comparable (Table 2) to the weight of the 4.05 Å phase in each sample as determined by XRPD. Furthermore, subsequent XRPD analyses made on the treated samples showed that the 4.05 Å peak had completely disappeared in most of the samples (Fig. 3), especially in those whose XRPD

characteristics most closely matched opal-CT, whilst all other phases appeared unaffected by the treatment. However, for the two samples RT7333 and RT7945, which both have much smaller FWHM values, a small peak remained at ~ 4.05 Å following NaOH treatment. Measurement of the FWHM of this residual peak showed that it was 30% narrower than the FWHM of the peak prior to treatment, at 0.209 and $0.226 \Delta^\circ 2\theta$, respectively.

In contrast, the industrial cristobalites were largely insoluble when treated by NaOH. Indeed, one sample recorded a small weight gain, presumably due to gravimetric error. The largest weight loss recorded was $\sim 11\%$, and occurred for the cristobalite sample with the finest particle size, XPF6. Similarly, the natural high-temperature cristobalite, Cri-14, was largely insoluble, losing only 2.5% of its weight. The XRPD analysis determined that this sample contained only 40% cristobalite, equivalent to a 6.25% cristobalite loss, assuming that no feldspar was dissolved. Neither of the quartz samples was dissolved to any great extent. Of the five clay samples, STx-1 showed complete dissolution of the 4.05 Å phase. Chipera & Bish (2001) estimated that this clay contains $\sim 30\%$ opal-CT. The other four clay samples were included to assess the affect of the NaOH dissolution on clays *per se*. For the two smectites, the maximum weight loss was 3.7% (SAz-1),

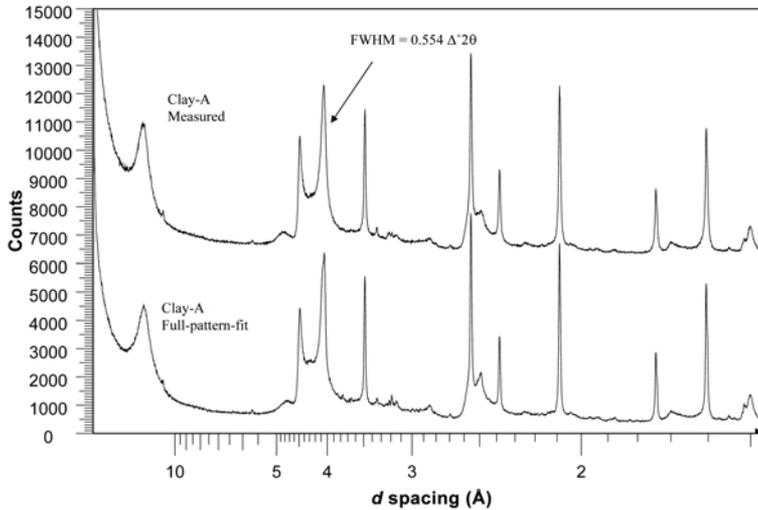


FIG. 2. Example of full pattern fitting of sample 'Clay-A'. In addition to the opal-CT (if classified based on the FWHM criteria of Elzea *et al.* (1994)) and dioctahedral smectite, both traces show peaks due to the 20% corundum added as an internal standard, as well as traces of quartz and feldspar.

whereas both kaolinites lost more weight, the finer grained kaolinite (KGa-2) losing just over 11%. The greater weight loss of the kaolinites is in keeping with the known greater solubility of kaolinite in NaOH compared with montmorillonite (Hashimoto & Jackson, 1960; Carroll & Starkey, 1971).

DISCUSSION

NaOH has been used previously by several authors (Foster, 1953; Hashimoto & Jackson, 1960; Jones, 1969; Müller & Schneider, 1993) to dissolve opaline silica from clay materials. Foster (1953) seems to have been the first to suggest the use of

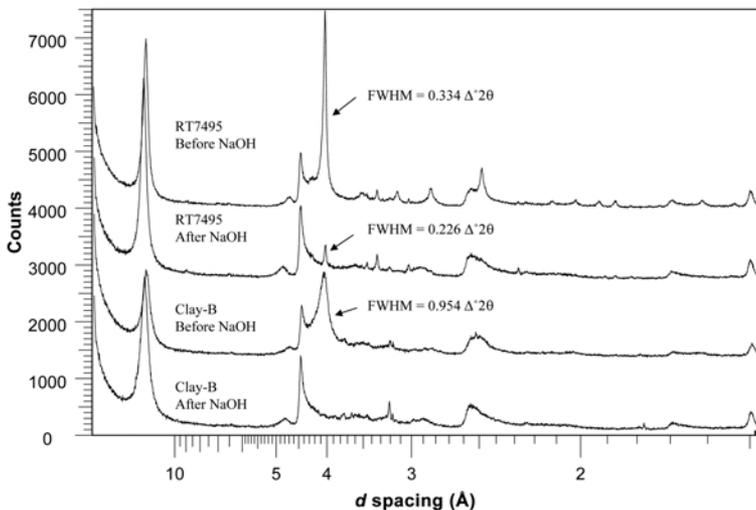


FIG. 3. Samples Clay-B and RT7495, before and after treatment with 0.5 M NaOH. In Clay-B all traces of the opal-CT are removed by the treatment. In RT7495 a small residual sharper peak remains near 4.05 Å. This peak may indicate that a small fraction of this sample has closer affinities with crystalline cristobalite, which is less soluble under the test conditions.

NaOH to dissolve free silica impurities in clay mineral samples prior to chemical analysis. She tested various materials and recommended a procedure using 1 g of sample reacted with 75 ml of 0.5 M NaOH on a steam bath for 4 h. She showed that this procedure was sufficient to dissolve up to 400 mg of opal but only 7.5% of a bentonite clay over the 4 h period. Subsequently, Hashimoto & Jackson (1960) further investigated the use of NaOH as a means of purifying clays. They discovered that a treatment by boiling in 0.5 M NaOH for as little as 2.5 min was effective in the removal of large quantities of free silica. Jones (1969) also used NaOH to determine the content of biogenic opal phytoliths in soil and Müller & Schneider (1993) developed an automated procedure for the determination of opal in deep-sea sediments based on dissolution in 1 M NaOH at 85°C. As with most selective chemical dissolution procedures (Smith & Mitchell, 1987), selectivity is dependent both on the characteristics of the material examined, such as SSA, as well as details of the procedure itself, such as reaction time, etc.

In unreported tests made prior to the present investigation, we found that the procedure of Hashimoto & Jackson (1960) dissolved a smaller percentage of the cristobalite specimens but was not of sufficient duration to completely dissolve the opal-CT phase in the various bentonites tested, as indicated by XRPD. Increasing the reaction time to 10 min, as reported herein, resulted in complete dissolution of the opal-CT in bentonites, but with a trade-off of increased dissolution of the cristobalites. Nevertheless, the maximum amount of any cristobalite solubilized at ~11% is far less than that recorded by Miles (1994) who used the refluxing phosphoric acid procedure, detailed in NIOSH 7601. With the latter procedure Miles (1994) showed that three standard cristobalites were all solubilized by amounts ranging from 17.4–27.6%. Furthermore, Miles (1994) also recorded 11.5% dissolution of a standard quartz. In the study by Miles (1994) the standard cristobalite showing 27.6% dissolution is the Gem Dugout (Deane K Smith) standard. This standard was also tested in the present investigation and showed <1% dissolution. In addition, the quartz standards tested in the present investigation by the NaOH procedure showed <2% dissolution. The geochemical modelling software *Visual MINTEQ* (Gustafson, 2005), which incorporates mineral solubility equilibria, was used to calculate the solubility of amorphous

silica, cristobalite and quartz at 100°C in NaOH of variable molarity. The solubility constants for all three phases were taken from Lindsay (1979). These calculations show that, in theory, 5 g of either amorphous silica, cristobalite or quartz would all be completely soluble in 500 ml (0.166 mol l⁻¹) of 0.5 M NaOH at 100°C (Fig. 4). This emphasizes that in essence the NaOH method described here relies on differences in kinetic factors that affect the rate of dissolution.

The results of the quantitative XRPD of the opal-CT and opal-C in the bentonite and clay samples (Clay-A, Clay-B, Clay-C, RT4733, RT4795, Pre-ship-T-16, STx-1) correspond very closely with the weight losses observed following the NaOH treatment. Assuming that the XRPD data are reasonably accurate, this correspondence indicates that the NaOH treatment can be used as a simple method to quantify the amount of opaline silica in bentonite samples. This can be justified by the observations that montmorillonite standards (SWy-1, SAz-1) show only minor reactivity and that XRPD patterns measured after the treatment (e.g. as shown in Fig. 3) demonstrate that the opaline silica has been more or less completely dissolved.

The fact that cristobalite is not dissolved to any great extent indicates that the NaOH procedure is also well-suited as a practical method for distinguishing cristobalite from opal based on differences in their chemical reactivity. Our data suggest that opal-CT will be completely dissolved, even when it accounts for more than half of the sample, leaving no ambiguity in its identification in bentonite. Perhaps the only caveat would be if a fine grained intergrowth with other minerals such as feldspars physically prevented the dissolution of

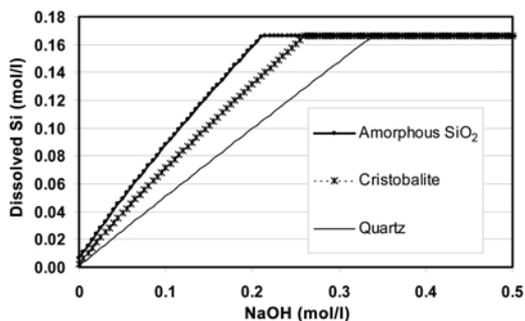


FIG. 4. Calculated solubility of SiO₂ phases (10 g l⁻¹) in the presence of varying concentrations of NaOH at 100°C.

opals; an issue for any dissolution-based method. Similarly, opal-C is almost completely dissolved by the NaOH procedure. The presence of some unreacted material with narrower XRPD peak widths in the opal-C samples suggests that a small, but measurable, fraction of this phase in these samples may be more closely allied to cristobalite. Such observations lead us into the debate over whether or not the opaline forms of silica are completely distinct from cristobalite. On the one hand, some authors argue that opaline forms of silica are clearly different from cristobalite (Elzea *et al.*, 1994; Miles, 1994; Smith, 1998) and they imply that reports of cristobalite in bentonites may all be cases of misidentification. On the other hand, there is evidence from transmission electron microscopy that opal-C can contain domains of highly-ordered cristobalite (Elzea & Rice, 1996; Nagase & Akizuki, 1997). Since there is also evidence that opal-C may form at a higher temperature than opal-CT (Elzea *et al.*, 1994), it may be more realistic to view the opals as phases that are transitional to cristobalite (Elzea & Rice, 1996). From this point of view, natural examples may display a range of properties related to the extent of their opaline vs. non-opaline character, as expressed for example by differences in their XRPD patterns and chemical reactivity.

With the likely prospect of further regulations in relation to crystalline silica, simple but reliable methods are required to distinguish crystalline forms from opaline forms, particularly opal-CT and opal-C from cristobalite in industrial materials such as bentonites. The XRPD analysis has shown some promise in this respect (Elzea *et al.*, 1994), but it would be unwise to rely on XRPD data alone. Indeed, all six of the cristobalites studied here have FWHM values that fall outside the range suggested by Elzea *et al.* (1994) for cristobalite but are within the range given for opal-C. We have shown that a selective chemical dissolution procedure based on treating 5 g of sample in 500 ml of 0.5 M NaOH at 100°C for 10 min is a simple and effective procedure that could be used in support of XRPD analysis. As with any selective chemical method, discrimination is operationally defined. It would nevertheless be much easier to apply such a method in relation to a regulatory framework compared to methods with more of an interpretive element like XRPD, where the judgement and experience of the operator are important. Lastly, the driving issue behind the interest and concern over crystalline

silica is its biological reactivity and it is well known that different samples of the same form e.g. quartz, may have very different reactivity (Wendlandt *et al.*, 2007; Fubini & Fenoglio, 2007). With the opals and cristobalite we have the added complexity of finding ways to consistently identify and classify them in the first instance so that meaningful comparisons of different samples can be made. The NaOH method advanced here is simply another tool in this respect.

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